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COUNTRY	USSR	DATE OF INFORMATION	1950
SUBJECT	Scientific - Metals, electron microscopy		
HOW PUBLISHED	Monthly periodical	DATE DIST.	26 Jan 1952
WHERE PUBLISHED	Moscow	NO. OF PAGES	14
DATE PUBLISHED	Nov 1950		
LANGUAGE	Russian	SUPPLEMENT TO REPORT NO.	

THIS IS UNEVALUATED INFORMATION

SOURCE Zavodskaya Laboratoriya, No 11, 1950, pp 1321-1330,

INVESTIGATION OF THE STRUCTURE OF METALS WITH AN ELECTRON MICROSCOPE

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/Diagrams referred to are appended/

High resolving power and the possibility of obtaining high magnifications have created broad perspectives for the use of the electron microscope in investigating the fine structure of metals. However, with electron microscopy at its present level, the investigation of metal structure still presents a very complex problem.

The qualitative preparation of the metal objects requires extremely careful and sometimes highly specialized methods.

A poorly prepared specimen may give a completely distorted picture. Inaccurate methods, not assuring that the field of view will include a given part of the structure, will not allow the researcher to accurately interpret the results and may lead to erroneous conclusions. The lack of effective utilization of the electron microscope to solve metallurgical problems, up to the present time, has in part been caused by the complexity of preparing and examining the specimens.

Such a position is not in keeping with the potentialities of electron microscopy and must be altered through the mastering of methods for preparation and examination.

The possibilities of the electron microscope are determined starting from the actual resolving capacity which, under normal conditions is about 50A. This resolving capacity may be used if the specimen model reproduces

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the details of the surface structure of the specimen being studied with an equal or higher degree of accuracy. However the methods of transferring a specimen's structure by presently-known methods assures a resolution of only about 100A (0.01μ).

The electron microscope may be used to study (1) form and dimensions of certain submicroscopic crystals, (2) figures of deep etching, (3) effect of various etchants (4) mechanism of deformation and breakdown, (5) process of recrystallization (6) phase conversions in heat treatment, (7) kinetics and products of dispersive decomposition (heat-resistant, high-strength, highly-coercive alloys), (8) processes occurring on grain boundaries, (9) mechanism of crystallization, (10) diffusion in chemico-thermal processing, etc.

Problems 1-5 involve study of the over-all picture of the metal's structure. Problems 6-8 require viewing certain details of the structure; and 4, 9, and 10 require also a representation of the trend of the process.

Only the first of these problems may be solved by the direct method used in the study of transparent specimens. Solution of the other problems requires indirect methods of study on special models of the specimen surface, especially prepared by polishing (mechanical or electrolytic) and etching.

Electrolytic polishing has substantial advantages over mechanical polishing.

After polishing, the specimen to be used for exposing structural components is subjected to chemical or electrolytic etching. Here, multiple polishing and etching is frequently necessary to bring out the true structure of the metal.

Electrolytic etching is generally conducted in the same electrolyte used for the polishing operation, but with reduced current density; and, in many cases, gives good results.

In the electron microscope, a contrast image may be obtained only if the model is taken from a surface of the specimen having a relief. (To obtain an oxide film representing not the model but an extremely fine slice of the section, the etching requirements are somewhat different, and a relief is not always necessary.)

This relief should be neither too deep nor too shallow -- it being difficult in the first instance to take from the specimen an intact model; and in the second instance the image contrast would be low. The etchant, therefore, is of the greatest importance. The dissolving rates of the different structural components in a given etchant must vary sufficiently; and, in addition, the etchant must not form surface films or spots on the specimen which cannot be removed in subsequent washing. The examiner should be oriented on the structural components designated for study. These components will be visible under the optical microscope following their coalescence as a result of heat treatment. The height of the relief must be controlled. To this end, the surface of the specimen may be shaded by coating in vacuum with a thin layer of metal dust distinguishable by its color and applied obliquely. Coatings of copper, chromium and graphite have given excellent results on steel, babbits and aluminum alloys. When the shaded specimens are examined in a metal microscope the shadows of particles rising above the plane of the specimen's surface are distinctly visible (Figure 1). Knowing the angle of coating, it is not difficult, then, to calculate the height of the relief according to the length of the shadow.

From the specimen thus prepared, polished and etched in relief, extremely fine models are made for examination in the electron microscope. The models must comform to the following requirements:

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1. Models must be sufficiently thin and strong, permit examination in passing electron beams and not break down during examination. Permissible thicknesses lie between 0.05 and 0.07 microns.

2. The structure of the models themselves must not appear within the range of the electron microscope magnifications.

3. The models must give a contrast image of the surface structure of the specimen, and have the capacity to transmit details whose dimensions correspond to the microscope's resolving power.

4. The material of the film must not react chemically with the metal being studied.

Several methods have been widely used -- lacquer, quartz and oxide-film models -- all yielding a good reproduction of the metal structure.

The simplest procedure involves a negative lacquer model, e.g., using a 0.5-1% solution of "formvar" in dioxane, or collodion in amyl acetate.

However, lacquer models, being a negative copy of the relief, have considerable disadvantages. Because of incomplete wetting of the specimen's surface, fine details in the relief are "leveled down." The surface tension of the film also contributes to this. For this reason, lacquer models may reproduce with satisfactory contrast relief of medium depth only.

It is possible to amplify artificially the contrast of the image given by the lacquer film. To do this, the lacquer model is coated with a metal dust (e.g., gold or chromium) similarly as for the control of relief of the specimen surface.

On the photomicrographs obtained, the actual structure of the metals dusted on in a thin layer (gold-8A, chromium-70A) is not observed.

By using the shading method, it is possible to see the finest objects with great sharpness and contrast (Figure 2). It should be noted, however, that the properties of lacquer films are not outstanding; and the relatively low strength necessitates working at a minimum electron-beam intensity.

The properties of quartz models are incomparably higher, but obtaining the models is considerably more complex. However, the difficulty is completely overshadowed by the results obtained.

The quartz film is positive and is prepared in a two-stage operation. First, a negative impression is made in plastic. On this impression is placed a layer of quartz which, upon removal, is used as the specimen.

To do this, the sample is pressed into carbolite by a special method which allows multiple electrolytic polishing and etching of the specimen to establish the best system for etching in relief. The sample is placed with the specimen surface downward on an insert with a polished end, placed in the mounting form of a small laboratory press.

The form is then filled with carbolite powder to cover the sample, and a plunger is inserted. Pressure is exerted on the plunger, of the order of 180 kg/sq cm, and the form is heated to 80°. At this temperature, the pressure is increased to 350 kg/sq cm and heating is continued to 150°. After a short period, the form is cooled, the plunger is withdrawn and the sample, pressed in carbolite, is taken out.

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The carbolite is removed from the unpolished end surface of the sample and a piece of flexible copper wire about 20 cm long is soldered on. The carbolite is then removed from the specimen surface, and the sample is polished with emery cloth. The surrounding carbolite prevents burring of the specimen's edges.

After the sample is polished and etched, the attached wire is wound into a tight spiral, the backing ring is put on and the sample is placed in a form with the specimen surface up. Polystyrene powder is poured on the surface and the plunger is inserted. The form is heated to 130°; pressure is brought to 350 kg/sq cm, and temperature is raised to 160°. This temperature is maintained for a short time, after which the form is cooled to 80° while pressure is maintained in order to avoid bubble formation in the polystyrene model. At 80°, the form is opened and the model is removed from the specimen surface by light tapping. To facilitate removal of the model, a flat metal ring is placed on the carbolite before pressing.

The surface of the model represents a negative image of the specimen. Microscopic examination reveals the model to be a completely accurate "negative" reproduction of the specimen.

The surface of the polystyrene negative is carefully washed and dried, and then placed under the bell jar of a vacuum apparatus. A heater, in the form of a 10-mm high conical spiral of 0.5-mm wolfram wire, is attached 60-80 mm below the negative. Inside the heater and directly on the spiral turns are placed 1-2 mg of pulverized pure quartz.

At a vacuum of 10^{-4} mm Hg a current of 20-25 amperes is put through the heater. The spiral is thereby heated to a temperature of about 2000° and the quartz evaporates and settles in a very fine film on the polystyrene surface. The evaporation period is about one minute, during which time the polystyrene does not heat over 50°.

Due to the extremely high mobility of the condensed quartz, it fills in even the finest contour features in the relief of the negative.

After the negative is coated with the quartz, the quartz then is trimmed from the side and back with an abrasive. The quartz film is cut into four sections and the negative, with the relief turned up, is submerged in a flat glass cup with ethyl bromide. The polystyrene adheres to the bottom of the cup, begins to dissolve and after several minutes, the pieces of the quartz film come to the surface. The quartz models are recovered with a special spoon. Since they are difficult to see, side illumination is used with a red glass placed beneath the cup. They are then placed in a washing solution and placed on the diaphragm of a specimen holder.

The quartz models assure high image contrast. They are stable and reproduce the fine structure of the metal with a high degree of accuracy (Figure 3).

Oxide film models are particularly good with respect to reproduction properties. They are formed during surface oxidation of the metal. Excellent oxide films are obtained on aluminum and some of its alloys; and they may also be produced on a number of other metals, e.g., nickel and nickel alloys, and stainless steel.

Production of a film on aluminum and its alloys is accomplished by anodization-electrolytic oxidation, also used for protection from corrosion. Good results are obtained from the use of ammonium borate or double displaced sodium orthophosphate. In the latter case, the process of anodization takes 3-5 minutes at room temperature and about 20 volts. The formed oxide film

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is removed by the mercury method, in which the film, cut into four sections, is separated from the specimen surface during the soaking of the specimen in a mercuric chloride solution. The oxide film is of uniform thickness. Image contrast is determined by varying the inclination of individual parts of the film. The greater the angle, the longer the electron path in the film. On the screen, the darker portion of the image will correspond to the "steep" portions of the model.

During the formation of an oxide film on an alloy, the depth of the film may show greater second-phase particle dimensions, with the result that after the film is separated from the specimen, these particles will appear suspended through the film and will be visible when the model is viewed in the electron microscope.

Thus, the oxide film is not merely a model; it is rather a microsection of the specimen, reproducing not only the surface structure, but also the internal structure -- a characteristic not apparent in other types of models. An example of structure as observed using an oxide film appears in Figure 4.

The methods of preparing specimen-models of a metal surface are highly varied and are not customary for metallurgists. Moerover, not one of the methods is universal.

Using the methods described here, it is possible to solve only the simplest metallurgical problems, involving, fundamentally, the examination of an over-all picture of the surface structure.

Metallurgists, meanwhile, are faced with a number of more real and considerably more complex problems; i.e., studying the structure of tempered steels, high-strength aluminum alloys, heat-resistant, highly-coercive alloys, etc. The study of the kinetics of the decomposition of the solid solution and separation of dispersed particles in these alloys are essential to understanding the nature of their properties.

When examining the details of a complex structure, it is sometimes extremely difficult to interpret the picture observed.

It is expedient to undertake a gradual transition from low to high magnifications, following the step-by-step appearance of new details in the image.

However, this is not the only point. In order to examine the structure of a certain particle, the electron microscope must be used. This process is complicated by the fact that for "medium" magnifications (10,000-20,000) the diameter of the field of view is about 6 μ

It is indisputably necessary that there be a more complete methodology for the preparation of microscope specimens, assuring accurate placement of the film on the object diaphragm and coincidence of the portions of the surface examined in electron and optical microscopes.

The "sighting" method developed by the authors gives excellent results. It is designed for all forms of specimens, uses the standard object diaphragm, has no adverse effect on the film's properties. The accuracy of mounting the specimen is determined by the accuracy with which the tube of the optical microscope is manipulated in adjusting the specimen and the diaphragm.

With this method, it is possible to examine the structure of a single component in electron and optical microscopes, to observe the structure of any zone designated, the grain boundary, etc. The method is a universal one, applicable to all forms of presently known specimens -- quartz, lacquer, and oxide films -- and permits the study of the fine structure of complex alloys.

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The specimen surface to be studied is polished, etched and examined under an optical microscope. The required point on the surface (structural component, portion of grain boundary, etc.) is brought under the intersection of the crosshairs in the eyepiece. Then, by turning the eyepiece or stage, coincidence of movement of the stage with direction of the crosshairs is established. The designated spot on the surface in then moved slightly along one of the hairs; the object lens is then replaced by a diamond marker which is brought to bear on the specimen surface. By moving the stage a fine graduation line is produced in a direction away from the designated point. With the object lens back in place, the accuracy of the line is checked. Its "indicating" end should be 0.1-0.15 mm from the designated point. The operation is then repeated, the second line being drawn perpendicular to the first. The result is two fine, mutually-perpendicular lines whose projections intersect at the structural detail to be examined. To facilitate the finding of a designated section it is marked with a circular line using the same diamond.

Other methods may be used to mark a specimen surface. If, for example, four impressions are made with the indenter of the apparatus for measuring microhardness, the impressions being made along the crosshairs around a designated point, these impressions can be used to locate the point.

The lacquer, oxide, or quartz films are then prepared by the usual methods from the marked surface. Preparation of the quartz film is a two-stage process, the impression first being obtained on a thin polystyrene disc which is then coated in vacuo with quartz.

In contrast with generally accepted methods, the oxide and lacquer films, after separation from the specimen surface, are also mounted on polystyrene plates. Thin (0.15-0.2-mm thick) transparent discs, from which are cut rectangular plates, are specially pressed out of polystyrene. The oxide and lacquer films are removed from the wash bath on these plates.

Thus, all three types of film evolve as a universal microscope specimen with a polystyrene base (Figure 10).

Either of the specimens is placed on the stage of a biological microscope with the film down, the specimen forming a bridge between two specimen slides so that the film does not touch the slides. The film structure is examined through the polystyrene plate at about a 400-x magnification. Moving the stage and orienting by the easily visible small circle, the impressions or lines are aligned with the crosshairs, the designated structural component then falling in the optical axis of the microscope (Figure 11 a).

Details of the metal structure, the indenter's impressions and the lines are discernible on the film in the optical microscope, but image contrast is low because of the slight thickness of the specimen. All details are easily discernible when the film is sprinkled with water.

To the microscope's object lens housing is affixed an accurately fitted collar of organic glass with an aperture under the front element of the object lens and with a flat end surface (Figure 8 b). Glue is applied to the end surface of the collar, and the microscope tube is carefully brought into contact with the polystyrene plate which adheres to the collar and is raised by reversing the motion of the tube (Figure 8 c).

An object diaphragm with a circular aperture 0.2-0.25 mm in diameter is placed on the specimen glass with the aperture centered on the crosshairs while viewing the diaphragm through the specimen. The edge of the diaphragm is also coated with an adhesive (e.g., starch gum). The tube is again lowered so that the diaphragm presses against the specimen and is held thus for several minutes (Figure 8 e). The tube is then raised and the specimen, glued to the diaphragm, is carefully removed from the end of the collar with tweezers.

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The polystyrene plate is dissolved in ethyl bromide (film and adhesive do not dissolve). The diaphragm and film are washed and mounted in the specimen holder (Figure 8 f).

An example of the "sighting" method is shown in Figures 5 and 6. For a more complete understanding of the process of deformation of the cementite in the example shown, the picture must be oriented according to the direction of action of the forces. This may also become necessary in other cases; e.g., orientation according to direction of heat elimination, direction of the diffusion process, etc.

For this purpose, a special mark is produced on the specimen surface (Figure 12). Then the film is made and joined with the diaphragm, on the surface of which a radial line has been marked. The diaphragm is so oriented that this line coincides with the direction as marked on the specimen. When inserting the cartridge with the specimen in the object chamber, the position of the line and, therefore, of the specimen is noted. At a given magnification, the angle of rotation of the image in the microscope may be measured. The specimen is first examined at the magnification, oriented, and then as the magnification is changed, further rotation of the image is considered.

It is best to use the "sighting" method in combination with the panoramic exposure method.

Structure details observed in the electron microscope frequently are not covered in the field of view. Consequently, when examining photographs of individual portions of the specimen it is sometimes difficult to interpret the picture obtained. But by photographing a certain area of the specimen, taking a series of overlapping pictures and then mounting them as a single panorama, that picture will be incomparably clearer. Thus, the structure of cast aluminum shown in Figure 8 is difficult to understand. The panoramic electron photomicrograph in Figure 7 shows that this fragment of a dendrite branch is with a portion of branch of a higher series (shown by the arrow). The panorama clearly shows the mosaic structure of the dendrite, the irregularity of its growth and the formation system of the branches. The panoramic electron photomicrograph of deformed aluminum, shown in Figure 9, is also of interest. It shows that dendrite is deformed nonuniformly. Together with zones where the structure of the cast metal is preserved, there are visible highly deformed zones.

It should be noted that the panoramic photograph requires a large number of exposures (sometimes up to 100) from one specimen, under constant conditions. Modern electron microscopes, requiring evacuation after each reloading of the camera, have an extremely low productivity.

Cameras designed to take a load of several plates offer no more than a partial solution to the problem inasmuch as such a system does not permit selective development of any one plate or control of negative quality.

The making of a complex panoramic photograph sometimes necessitates wasting many hours because of the great inconveniences. For this reason the problem of designing a high-output apparatus for continuous operation, which will allow rapid reloading and the development of any plate immediately after exposure, is significant.

One of the most complex problems is the investigation of processes of structure formation, starting with the separation of the finest particles (complex carbides, intermetallic compounds). Such structures are formed during the heat treatment of steels, high-strength aluminum alloys, heat-resistant, highly-coercive, and other alloys.

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The study of these processes is generally conducted by way of comparing an initial structure (e.g., after tempering) and a number of intermediate structures (after annealing at various temperatures). In examining the specimen from a sample of a special nickel-base alloy, the characteristic structure of a single-phase solid solution is visible after tempering. It is possible to observe corrosion of the grain, obviously, along the boundaries of the mosaic blocks.

A completely different structure is visible in the electron photomicrograph in Figure 13, where the separated particles show up. It is noted that these particles are distributed not irregularly but somewhat in the form of a screen -- which is also obviously connected with the mosaic structure.

Comparing the structures of the alloy after tempering at various temperatures, it is subsequently possible to observe the appearance of extremely fine segregations, their coalescence and transition into the solid solution. It is also possible here to study directly the form and dimensions of the separated particles in isolated form. By electrolytic dissolving of the alloy base, the insoluble particles may be precipitated onto a structureless film and examined in the microscope. Comparison of the form and dimensions of the directly observed particles with particles visible on the model allows a more accurate interpretation of the picture. However, it must not be forgotten that such small particles collect in clots and chains, and it is therefore necessary to take special measures to prevent this (e.g., select a suitable medium). Disregarding these measures may lead to considerable distortion of the picture, as shown in Figure 14 (Mala and Nilsen, Metallurgy, 40, No 240, Oct 1949).

This photograph, as the authors of the article affirm, shows the structure of carbides remaining after the dissolving of stainless steel. However, upon close examination of the picture it is seen that it shows garlands of conglomerate particles of carbides.

The particles of the hardening phase (Figure 15) show up entirely differently (sample from Figure 13). The particles are easily discernible, even individually. The coincidence of the form and dimensions of the isolated particles with the structure as seen on the corresponding surface specimens is a good indication of the accuracy of the picture reproduced by the specimen models.

The examples given here show that the method can be used to obtain excellent electron photomicrographs.

However, for the metallurgical researcher, there remains the problem of interpreting the picture, and even with the simplest of structures, everything on the electron photomicrograph will not be clear. Thus, there may be gray and black bands which do not appear as shadows. In some cases, these bands may be interpreted as fissures. In Figure 16, for example, a large part of the picture field is covered by shaded figures of irregular form. The great depth of field of the image, inherent in the electron microscope, gives the picture a three-dimensional quality, resulting in the figures' being taken for fissures. Particularly interesting is the fissure beginning at the center of the picture and running to the right. The coincidence of the form of the edges of the fissure in the center and also the equivalence of the angles between the edges of the fissure and the rim of the dendrite branch are notable. To verify this, the picture was cut along the upper edge of the fissure. The upper portion of cracked branch was rotated clockwise through the angle (alpha) and put "in place". The rim of the upper portion of the branch then matched the rim of the lower portion (Figure 17), and the edges of the fissure in the center closed perfectly. It is possible to assume the presence of brittle fracture in such a plastic material as pure aluminum. At the same time, the fissure going from the center to the right is not closed. Evidently, plastic deformation occurred at this point, ending in viscous fracture. This manifestation of two forms of fracture in such close proximity and on such a plastic metal as aluminum is a fact which requires close study.

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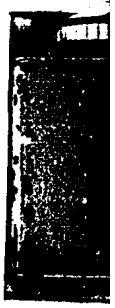
The possibilities for solving metallurgical problems with the use of the electron microscope are not exhausted by the examples given here. However, they are sufficient to allow the conclusion that with further development and skillful use of the methods, and systematization of investigations, the electron microscope will allow the revelation of much that is new and interesting concerning the structure of metals and alloys.

[See figures on following pages.]



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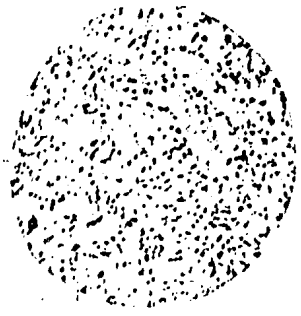

Fig. 1. Carbon steel; carbides, etched with nitric acid, shaded with copper. X 200

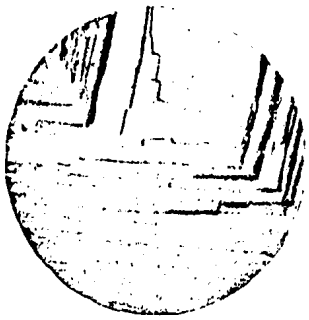

Fig 3. Pure aluminum. Oxide film. Electron photomicrograph. X 15,000.

Fig. 2. Steel 40. Lacquer film shaded with chromium. Electron photomicrograph. X 15,000

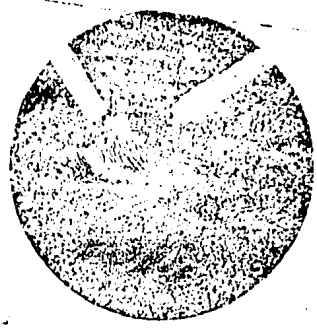

Fig. 5. Eutectoid steel, cold rolled; Surface marked for sighting method. X 200.

Fig 4. Luminar perlite in eutectoid steel. Quartz film. Electron photomicrograph. X 15,000.

Fig 6. Plastically deformed cementite. Quartz film. Prepared by sighting method from sample in Fig. 5. Electron photomicrograph. X 15,000.

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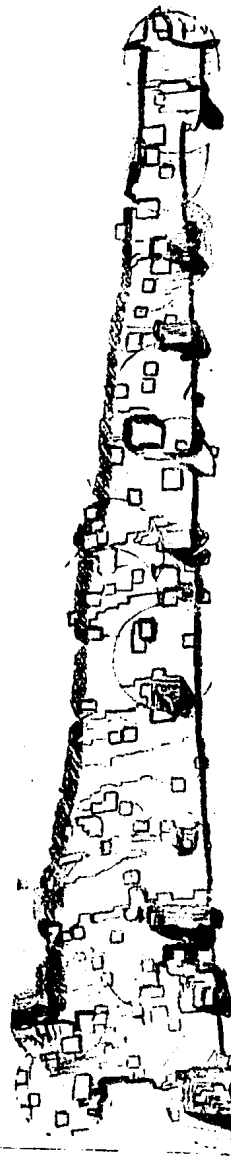

Fig. 7. Dendrite branch in cast aluminum. Oxide film. Panoramic electron photomicrograph. X 10,000. Reduced 3 times.

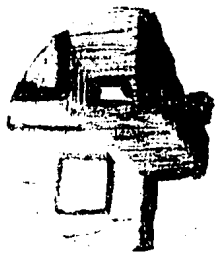

Fig 8. Fragment of dendrite branch in cast Al. Oxide film. X 12,000

Fig. 9. Dendrite in aluminum after hot pressing. Oxide film. Panoramic electron photomicrograph. X 12,000. Reduced 3.5 times.

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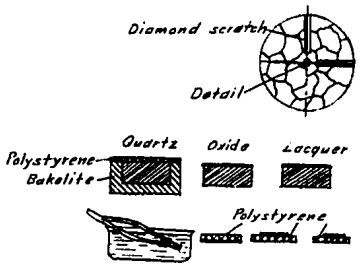

Fig 10. Preparation of specimens by the sighting method.

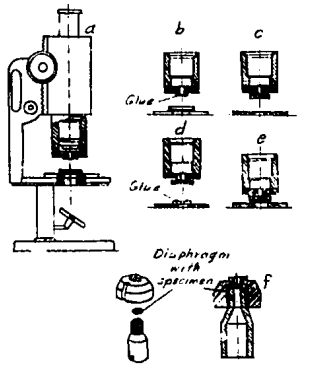

Fig 11. Adjusting specimens by sighting method.

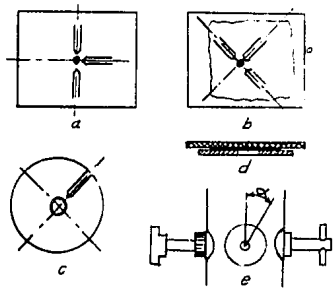

Fig 12. Method of orienting specimen by direction.

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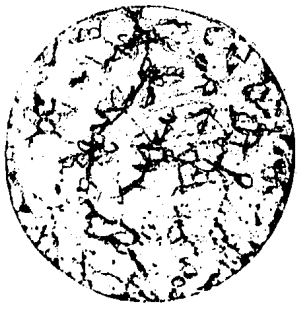

Ni-alloy. Tempered 900°.
Electrolytic etching.
Quartz film. X 15,000.

Carbide-particle garlands
in stainless steel.

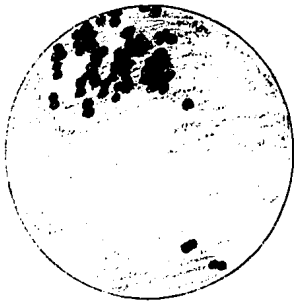

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Fig. 16

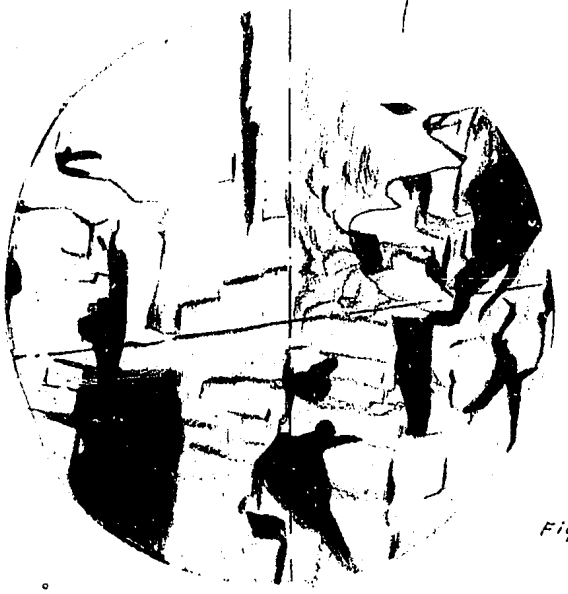

Fig. 17

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